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[19] THE PATENT OFFICE OF JAPAN (JP)
[12] OFFICIAL GAZETTE FOR UNEXAMINED PATENTS (A)

[11] Disclosure Number 5-302288
[43] Date of Disclosure November 16, 1993

[51] Int. Cl[5]	Identification Symbols	Intra-Agency File Nos.	FI	Technical Designation Here
D 21 C 9/16		7199-3B		
C 08 F 220/06	MLQ	7242-4J		
D 21 C 9/10	Z	7199-3B		
9/153		7199-3B		
//C 08 F 16/28	MKZ	6904-4J		

Request for Examination Not requested Number of Claims 8
(total 16 pages)

[21] Application Number 4-114853

[22] Filing Date May 7, 1992

[31] Number assigned to priority application 4-39805

[32] Date of filing of priority application February 26, 1992

[33] Country in which priority application was filed Japan (JP)

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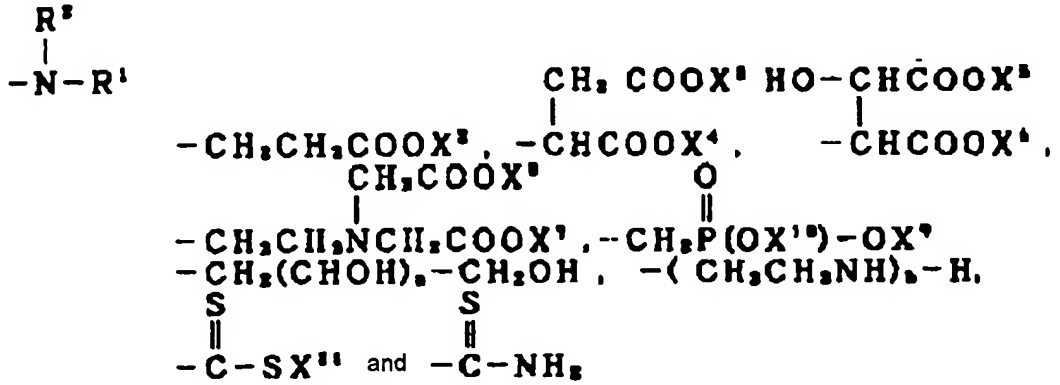
[54] Title of Invention
Method of pretreatment of wood pulp before bleaching

[57] **[Summary]**

[Structure]
A method of pretreatment of wood pulp before bleaching which uses water-soluble polymer having a structure represented by the following expression
[Fourth chemical formula]
(In the expression, R^1 and R^2 represent a substituent containing hydrogen or carbon, at least one of R^1 and R^2



X^1 to X^{11} represent hydrogen, monovalent metal, bivalent metal, inorganic or organic ammonium groups independently or together, and a as well as b represent an integer of 1 to 7.)

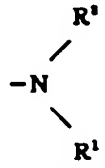
in the side chain for bleaching with peroxide bleach.

[Effect]

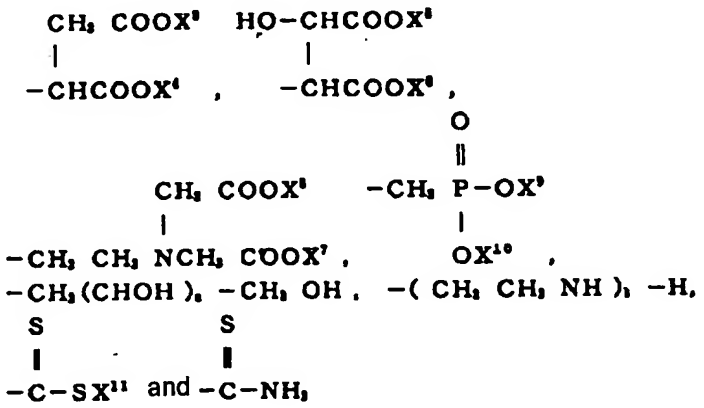
Wood pulp is subjected to bleaching pretreatment through inexpensive pretreatment having little toxicity, thereby permitting a high degree of bleaching of wood pulp in the subsequent bleaching step.

[Scope of Patent Claim]

[Claim 1] A method of pretreatment of wood pulp before bleaching which uses water-soluble polymer having a structure represented by the following expression



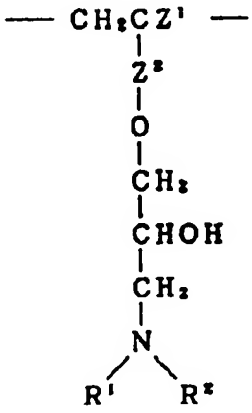
(In the expression, R^1 and R^2 represent a substituent independently containing hydrogen or carbon, at least one of R^1 and R^2 are selected from the group comprising



X^1 to X^{11} hydrogen, monovalent metal, bivalent metal, inorganic or organic ammonium groups independently or together, and a as well as b represent an integer of 1 to 7.)

in the side chain for bleaching with peroxide bleach.

[Claim 2] The method of pretreatment of wood pulp before bleaching of Claim 1 in which aforementioned water-soluble polymer contains structural units represented by the following expression

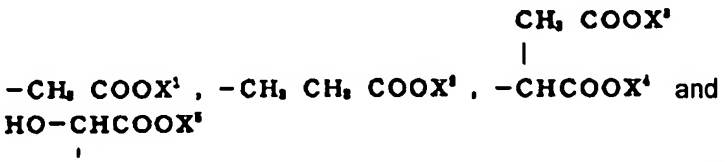


[First chemical formula]

(In the expression, Z^1 represents hydrogen or CH_3, Z^2 represents $-CH_2-$ or $-C-$
R^1 and R^2 have the same significance as above).

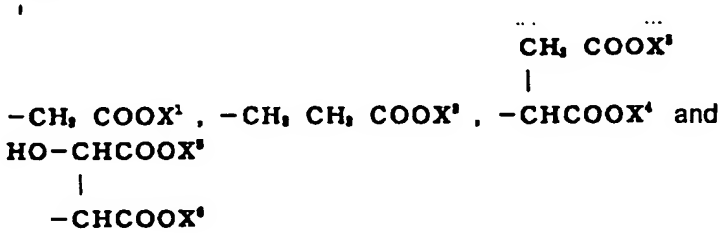
[Claim 3] The method of pretreatment of wood pulp before bleaching of Claims 1 and 2 in which at least one of R^1, R^2 in aforementioned water-soluble polymer is selected from the group comprising

(X¹ to X⁶ have the s



h R¹, R² independently or

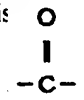
[Claim 4] The meth
together in aforeme



(X¹ to X⁶ have the same significance as above).

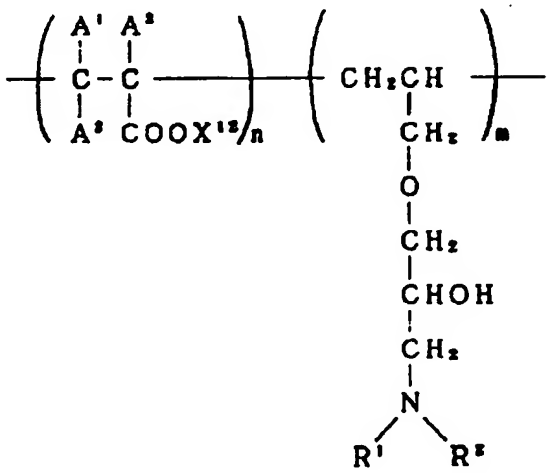
[Claim 5] The method of pretreatment of wood pulp before bleaching of Claim 4 in which Z^1 in aforementioned water-soluble polymer is hydrogen and Z^2 is $-CH_2-$.

[Claim 6] The method of pretreatment of wood pulp before bleaching of Claim 4 in which Z^1 in aforementioned water-soluble polymer is CH_3 and Z^2 is



[Claim 7] The method of pretreatment of wood pulp before bleaching of Claim 5 in which aforementioned water-soluble polymer is a copolymer represented by the following expression

[Second chemical formula]



(In the expression, A^1 and A^2 independently represent hydrogen, methyl groups or $-COOX^{13}$, but A^1 and A^2 concurrently do not represent $-COOX^{13}$, A^3 represents hydrogen, methyl group or $-CH_2COOX^{14}$ but A^1 and A^2 independently represent hydrogen or methyl group when A^3 represents $-CH_2COOX^{14}$, X^{12}, X^{13} and X^{14} independently or together represent hydrogen, monovalent metal, bivalent metal, inorganic or organic ammonium groups, R^1 R^2 have the significance as stated in Claim 5, n/m ranges from 20/80 to 98/2).

[Claim 8] The method of pretreatment of wood pulp before bleaching of Claims 1 to 7 in which aforementioned wood pulp is high-yield pulp.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Utilization] The present invention concerns a method of pretreatment of wood pulp that is carried

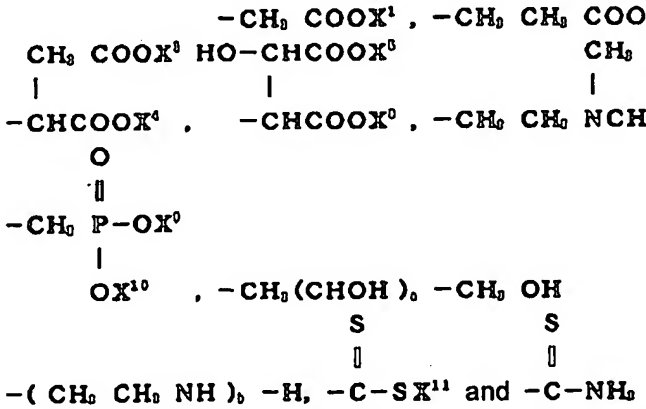
out before bleaching.
[0002]
[Prior Art] Wood pulp, for example, high-yield pulps including mechanical pulp (MP), groundwood pulp (GP), refining ground pulp (RGP), thermomechanical pulp (TMP), and chemomechanical pulp (CGP) are generally bleached with a peroxide-based bleaching agent such as hydrogen peroxide, sodium peroxide, peracetic acid or sodium percarbonate.

[0003] However, these peroxide-based bleaching agents are eluted by wood pulp during bleaching or they are decomposed by the catalytic action of polyvalent metals such as Mn, Cu, Fe, Ni, Co present in tap water and are uselessly consumed. Consequently, wood pulp is pretreated before bleaching to eliminate the adverse effects of these polyvalent metals.
[0004] This pretreatment commonly involves soaking wood pulp in a pretreatment bath comprising water or a pretreatment agent at a temperature range of room temperature to 70°C, followed by dehydration.
[0005] Pretreatment agents commonly used include aminocarboxylates such as ethylenediaminetetraacetate (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), diethylenetriamine penta(methylenephosphonic acid (DTPMPA) and condensed phosphates such as tripolyphosphates.
[0006]
[Problems Solved by the Invention] However, the use of aminocarboxylic-acid-based bleach pretreatment agents is restricted because they have little effect, are expensive and have comparatively strong toxicity. Furthermore, condensed phosphate-based bleach pretreatment agents cause red tide when they flow into the ocean through rivers as effluent.

[0007] Consequently, polycarboxylic acid-based bleach pretreatment agents have been proposed, as set forth in Japanese Kokai Publication Hei-1-266293, Japanese Kokai Publication Hei-1-266294 and Japanese Kokai Publication Hei-1-266295, to eliminate the problems associated with these aminocarboxylates and condensed phosphates.
[0008] However, these polycarboxylic acid-based bleach pretreatment agents have a comparatively good evaluation, but problems persist when obtaining vigorously bleached pulp.
[0009] The purpose of the present invention is to provide a method of bleach pretreatment of wood pulp before bleaching using bleaching agents such as hydrogen peroxide, sodium peroxide, percarbonate, perborate, peracetate, ozone and the like in which a pronounced pretreatment effect is attained inexpensively and with little toxicity even with comparatively low amounts of bleaching agent added.
[0010]
[Means of Solving the Problems] The method of bleach pretreatment of wood pulp in the present invention is one which uses water-soluble polymer having structural units (I) represented by the following expression

(I)

(In the expression, R^1 and R^2 represent a substituent containing hydrogen or carbon, at least one of R^1 and R^2 are selected from the group comprising



and

(A), X^1 to X^{11} represent hydrogen, monovalent metal, bivalent metal, inorganic or organic ammonium groups independently or together, and a as well as b represent an integer of 1 to 7.)

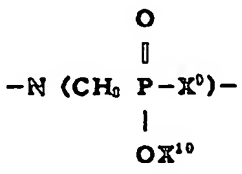
in the side chain for bleaching with bleaching agent.

[0011] A broad range of methods can be used without limitation to obtain aforementioned water-soluble polymer having structural unit (I) in the side chain.

[0012] For example, the structural unit can be obtained by ring-opening addition of polymers containing epoxy groups such as poly (meth) acrylglycidyl ether and polygylcidyl (meth) acrylate and acid anhydride-based polymers such as polymaleic anhydride using primary or secondary amines such as iminodiacetic acid (salt), iminodipropionic acid (salt), iminodisuccinate acid (salt), carboxymethyliminosuccinic acid (salt), hydroxyiminosuccinic acid (salt), N-methyl glycine (salt), dithiocarbamic acid (salt), thiourea and the like as raw materials.

[0013] In addition, it can, of course, be obtained by (co) polymerizing monomers obtained through ring-opening addition of monomers containing epoxy groups such as (meth) acrylglycidyl ether, glycidyl (meth) acrylate, etc., and acid anhydride-based monomers such as maleic anhydride using aforementioned primary or secondary amines.

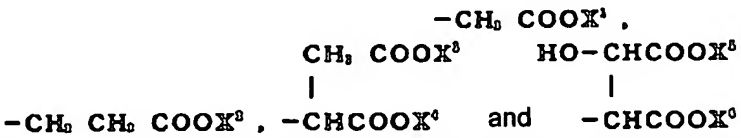
[0014] It can be derived using a water-soluble polymer having



in the side chain, for example, polymers having -NH- in the side chain along with formalin as well as phosphorus acid as the raw materials. In addition, it can be derived from monomers obtained using monomers having -NH- in the side chain and aforementioned raw materials.

[0015] Water-soluble polymers having structural unit (I) comprising polymers and monomers in the side chain can be produced through dehydrochlorination reactions, esterification reaction and the like.

[0016] At least one of R^1 and R^2 in structural unit (I) must be selected from among aforementioned substituent group (A), but the selection of any of the following from among (substituent group (B))



is desirable to enhance the chelating capability of the resulting water-soluble polymers to various types of polyvalent metal ions.

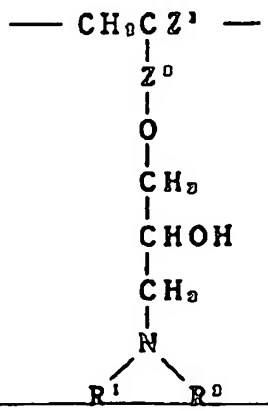
[0017] Furthermore, substituent group (B) can easily be inducted into water-soluble polymers, and that is desirable for obtaining inexpensive water-soluble polymers.

[0018] The selection of both R^1 and R^2 from among substituent group (B) is even more desirable for further enhancing the chelating capability of the resulting water-soluble polymers.

[0019] As mentioned above, there are various aforementioned water-soluble polymers having structural unit (I) in the side chain, and the inclusion of structural unit (II) represented by

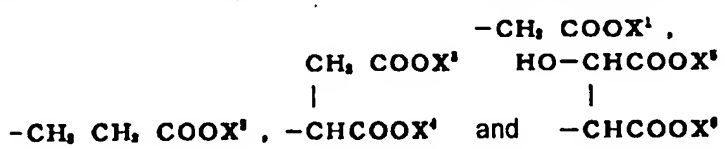
[0020]

[Third chemical formula]

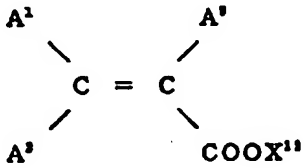


(II)

[0021]
(In the expression, Z^1 represents hydrogen or CH_3, C^2 represents $-CH_2-$ $\left(-\overset{O}{\overset{\|}{C}}-\right)$
and R^1 as well as R^2 represent a substituent independently or together selected from the group comprising



X^1 to X^6 have the same significance as above) is preferable.
[0022] Water-soluble polymers in which Z^1 is hydrogen and Z^2 is $-CH_2-$ are especially desirable since they are inexpensive and can be used even under severe (high-temperature) conditions.
[0023] There is no specific limitation to the proportion of structural unit (II) in water-soluble polymers, but a range of 2 to 80 mol% is preferable if Z^2 is $-CH_2-$. Furthermore, a range of 4 to 100 mol% is preferable $\left(-\overset{O}{\overset{\|}{C}}-\right)$
Water-soluble polymers that deviate from this range of proportions tend to have lower bleaching properties.
[0024] There is no specific limitation on the comonomer constituent if water-soluble polymers containing structural unit (II) serve as copolymers, and a broad range of monomers can be used.
For example, unsaturated carboxylic-acid monomers (III) represented by expression



(III)

(In the expression A^1 and A^2 independently represent hydrogen, methyl groups or $-COOX^{13}$, but A^1 and A^2 concurrently do not represent $-COOX^{13}$, A^3 represents hydrogen, methyl group or $-CH_2COOX^{14}$ but A^1 and A^2 independently represent hydrogen or methyl group when A^3 represents $-CH_2COOX^{14}$, X^{12}, X^{13} and X^{14} independently or together represent hydrogen, monovalent metal, bivalent metal, ammonium groups or organic amine groups). can be used. [Examples of such unsaturated carboxylic-acid monomers (III) include acrylic acid, methacrylic acid, crotonic acid, or these acids that have been partially or completely neutralized by monovalent metal, bivalent metal, ammonia, organic amine, (anhydrous) maleic acid, itaconic acid, fumaric acid, citraconic acid, or these acids that have been partially or completely neutralized by monovalent metal, bivalent metal, ammonia, organic amine. Monovalent metals include sodium and potassium. Bivalent metals include calcium and magnesium. Organic amines include alkyl amines such as monomethyl amine dimethyl amine, trimethyl amine, monoethyl amine, diethyl amine, and triethyl amine; alkanol amines such as monoethanol amine, diethanol amine, triethanol amine, monoisopropanol amine, dimethyl and ethanol amine; and pyridine. Among these, sodium is most desirable in that it is inexpensive and readily available on an industrial scale]; Also included are amide-based monomers such as (meth) acrylamide and t-butyl (meth) acrylamide; hydrophobic monomers such as (meth) acrylic acid esters, styrene, 2-methyl styrene, vinyl acetate; unsaturated sulfonic-acid-based monomers such as vinyl sulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, styrene sulfonic acid, 2-acrylamide-2-methyl propane sulfonic acid, 3-allyloxy-2-hydroxypropane sulfonic acid, sulfoethyl (meth) acrylate, sulfopropyl (meth) acrylate, 2-hydroxysulfopropyl (meth) acrylate, sulfoethyl maleimide or these acids that have been partially or completely neutralized by monovalent metal, bivalent metal, ammonia, organic amine; unsaturated monomers containing hydroxyl groups such as 3-methyl -3-butene-1-ol (isoprenol), 3-methyl-2-butene-1-ol (prenol), 2-methyl-3-butene-2-ol (isoprenalcohol), 2-hydroxyethyl (meth) acrylate, polyethyleneglycol mono (meth) acrylate, polypropyleneglycol mono (meth) acrylate, polyethyleneglycol monosioprenol ether, polypropylene glycol monoisoprenol ether, polyethyleneglycol monoallyl ether, polypropylene glycol monoallyl ether, glycerol monoallyl ether, hydroxyacrylic acid, N-methylol (meth) acrylamide, glycerol mono (meth) acrylate, and vinyl alcohol; cationic monomers such as dimethylaminoethyl (meth) acrylate and dimethyl aminopropyl (meth) acrylamide; nitrile-based monomers such as (meth) acrylonitrile; -olefin-based monomers such as ethylene, propylene, 1-butene, isobutylene -amylene, 2-methyl-1-butene, 3-methyl-1-butene (-isoamylene), 1-hexene, and 1-heptene. Among these, the use of unsaturated carboxylic-acid monomers (III) would be preferred.

[0025] There is no specific limitation on the molecular weight of water-soluble polymers, but a weight average molecular weight of 500 to 1,000,000 would be especially desirable. The bleaching properties in the bleaching step following pretreatment tend to fall since the chelating capability falls if the weight average molecular weight is below 500. Conversely, the bleaching properties tend to fall because water-soluble polymers readily undergo gelation due to polyvalent metal ions if the weight average molecular weight exceeds 1,000,000.

[0026] The water-soluble polymers in the present invention are polymers whose solubility in water is 1% or more. Both acidic and basic types may be used. Basic types include monovalent metal, bivalent metal, inorganic or organic ammonium salts.

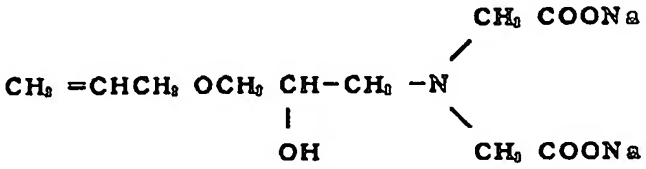
[0027] Examples of monovalent metal salts include sodium salts, potassium salts, and lithium salts. Examples of bivalent metal include calcium salts and magnesium salts. Examples of inorganic or organic ammonium salts include alkylamine salts such as ammonium salts, monomethylamine salts, dimethylamine salts, trimethylamine salts, monoethylamine salts, diethylamine salts, and triethylamine salts; alkanolamine salts such as monoethanolamine salts, diethanol amine salts, triethanol amine salts, monoisopropanol amine salts, and dimethylethanol amine salts; pyridine salts, etc. Among these, sodium is most desirable in that it is inexpensive and readily available on an industrial scale.

[0028] Furthermore, bivalent metal salts should total no more than 10 mol% of all carboxylic-acid groups to make the polymer water soluble.

[0029] Incidentally, the reason that an outstanding pretreatment effect is demonstrated when using the water-soluble polymers pursuant to the present invention as the bleach pretreatment agent is unclear, but the following is surmised. Specifically, the result of being able to remove polyvalent metals such as Mn, Cu, Fe, Ni, Co, etc., by dissolution suspension in pretreatment bath followed by dehydration when water-soluble polymers are used as bleach pretreatment agents is that the adverse effects of polyvalent metals is reduced in the bleaching step following pretreatment.

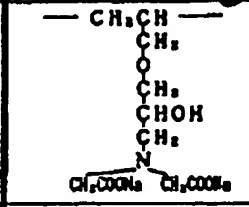
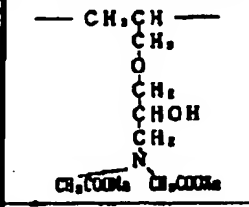
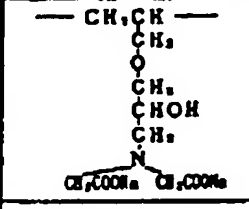
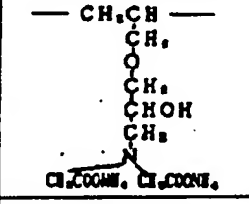
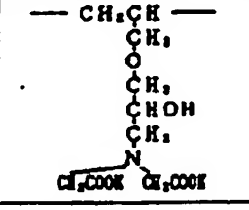
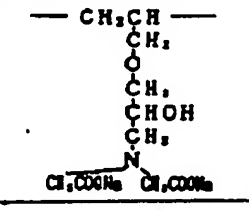
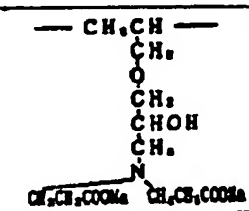
[0030] There is no specific limitation on the amount of water-soluble polymers used, but a range of 0.04 to 0.8 wt% per exsiccated pulp is common. The bleaching properties tend to decline if less than 0.04 wt% is used. No additional effect

commensurate with the increased amount is demonstrated if more than 0.8 wt% is used.
[0031] The water-soluble polymers pursuant to the present invention may be used in combination with bleach pretreatment agents that are conventionally used such as aminocarboxylates or condensed phosphates.
[0032] Furthermore, the method of bleach pretreatment pursuant to the present invention is not only effective on high-yield pulp, but it is also effective as a method of bleach pretreatment of various types of wood pulp including de-inked pulp (DIP), kraft pulp (KP), and soda pulp (AP).
[0033] In addition, chlorine-based bleaching agent used as the bleaching agent in the bleaching step following pretreatment would be effective using the bleach pretreatment method pursuant to the present invention.
[0034]
[Working Examples] The present invention is explained concretely below through examples. However, the present invention is not restricted to these examples. The parts and percentages in the examples denote weight parts and wt%.
[0035] Production method of water-soluble polymer 1
A total of 433.8 parts of ion-exchange water, 429.6 parts of 48% sodium hydroxide and 342.9 g of iminodiacetic acid were fed into a two-liter glass reactor fitted with a stirrer and condenser. After holding at a temperature of 65°C while stirred, 293.7 parts of allylglycidyl ether were added slowly over the course of 60 minutes using an instillation nozzle. After addition was completed, this was held for 30 minutes at the same temperature to complete the reaction.
[0036] This produced monomer (a) with an imino-di-structure represented by chemical formula



having 50% concentration.
[0037] Both 573 parts of a 50% aqueous solution of aforementioned monomer (a) and 449.5 parts of ion exchange water were fed into a two-liter glass reactor fitted with a stirrer and condenser and heated to 95°C. Next, 354.4 parts of 80% acrylic acid aqueous solution and 123.1 parts of 20% sodium persulfate aqueous solution were individually added slowly over the course of 60 minutes using separate instillation nozzles. This was then held for 10 minutes at the same temperature to complete polymerization.
[0038] Water-soluble polymer 1 comprising a monomer (a)/acrylic acid = 2/8 (molar ratio) copolymer was obtained. The total polymerization rate of water-soluble polymer 1 was 99 mol%. In addition, the weight average molecular weight was measured by water-based GPC and the results are presented in Table 1.
[0039] Water-soluble polymers 2 to 25 were obtained by the same method as that used for water-soluble polymer 1.

[0040]
[Table 1]

① 水溶性重合体番号	② 構造単位（I）を1個以上に含有する水溶性重合体			③ コハク酸成分	④ 比率*（mol%）	⑤ 塩の種類	⑥ 重量平均分子量
	構造式 ⑦	R^1	R^2				
1		$-CH_2COONa$	$-CH_2COONa$	⑧ アクリル酸	20	Sodium ナトリウム	98000
2		$-CH_2COONa$	$-CH_2COONa$	⑧ アクリル酸	3	Sodium ナトリウム	930000
3		$-CH_2COONa$	$-CH_2COONa$	⑨ マレイン酸	50	Sodium ナトリウム	5600
4		$-CH_2COONH_4$	$-CH_2COONH_4$	⑩ アクリル酸アンモニウム	10	Ammonium アンモニウム	800
5		$-CH_2COOK$	$-CH_2COOK$	⑪ メタクリル酸カリウム	30	Potassium カリウム	22000
6		$-CH_2COONa$	$-CH_2COONa$	——	100	Sodium ナトリウム	1600
7		$-CH_2CH_2COONa$	$-CH_2CH_2COONa$	⑧ アクリル酸	20	Sodium ナトリウム	86000

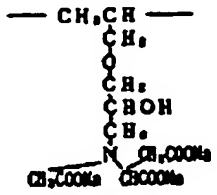
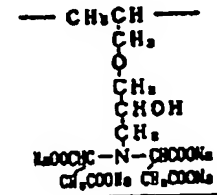
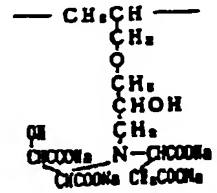
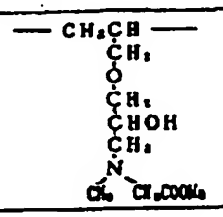
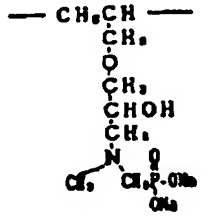
* 構造単位（I）を1個以上に含有する単量体の比率 ⑫

【0041】

[Table 2]

Key

1) Water-soluble polymer number
2) Water-soluble polymers containing structural unit (I) in the side chain
3) Comonomer constituent
4) Proportion* (mol%)
5) Type of salt
6) Weight average molecular weight
7) Structural formula
8) Acrylic acid
9) Maleic acid
10) Ammonium acrylate
11) Potassium methacrylate
12) Proportions of monomer containing structural unit (I) in the side chain

① 水溶性重合体番号	② 構造単位（I）を側鎖に含有する水溶性重合体 構造式 ⑦	R¹	R²	③ モノマー成分	④ 比率 * (mol%)	⑤ 塩の種類	⑥ 重量平均分子量
8		-CH_2COONa	CH_2COONa -CHCOONa	⑧ アクリル酸	20	Sodium ナトリウム	123000
9		CH_2COONa -CHCOONa	CH_2COONa -CHCOONa	⑧ アクリル酸	20	Sodium ナトリウム	94000
10		OH CHCOONa -CHCOONa	CH_2COONa -CHCOONa	⑧ アクリル酸	20	Sodium ナトリウム	74000
11		-CH_3	-CH_2COONa	⑧ アクリル酸	20	Sodium ナトリウム	27000
12		-CH_3	O -CH_2P-ONa ONa	⑧ アクリル酸	20	Sodium ナトリウム	18000
13		H	-C-SNa S	⑧ アクリル酸	20	Sodium ナトリウム	34000

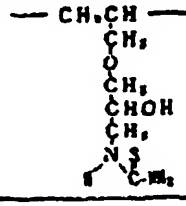
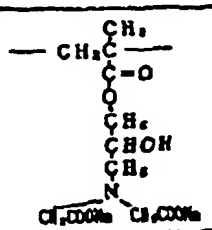
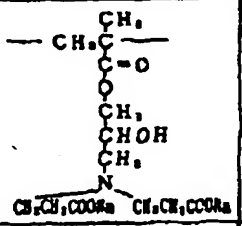
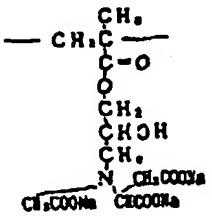
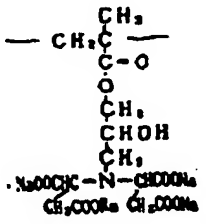
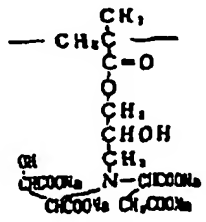
* 構造単位（I）を側鎖に含有する単量体の比率 ⑨

[Table 3]

【0042】

Key

1) Water-soluble polymer number
2) Water-soluble polymers containing structural unit (I) in the side chain
3) Comonomer constituent
4) Proportion* (mol%)
5) Type of salt
6) Weight average molecular weight
7) Structural formula
8) Acrylic acid
9) Proportions of monomer containing structural unit (I) in the side chain

① 水溶性重合体番号	② 構造単位（1）を必須に含有する水溶性重合体 構造式 ⑦	R¹	R²	③ モノマー成分	④ 比率 * (モル%)	⑤ 塩の種類	⑥ 重量平均分子量
14		H		アクリル酸 ⑧	20	Sodium ナトリウム	22000
15		$-CH_2COONa$	$-CH_2COONa$	アクリル酸 ⑧	20	Sodium ナトリウム	47000
16		$-CH_2CH_2COONa$	$-CH_2CH_2COONa$	アクリル酸 ⑧	20	Sodium ナトリウム	39000
17		CH_2COONa		アクリル酸 ⑧	20	Sodium ナトリウム	41000
18				アクリル酸 ⑧	20	Sodium ナトリウム	5700
19				アクリル酸 ⑧	20	Sodium ナトリウム	67000

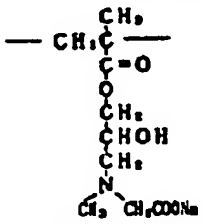
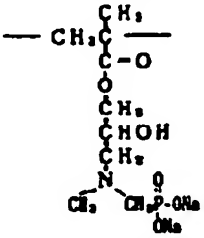
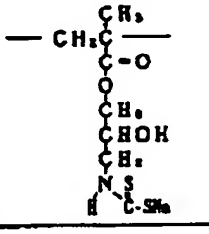
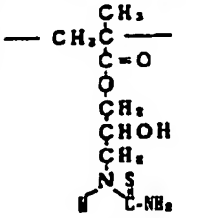
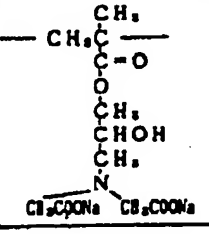
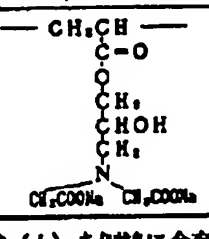
* 構造単位（1）を必須に含有する単量体の比率 ⑨

[Table 4]

【0013】

Key

1) Water-soluble polymer number
2) Water-soluble polymers containing structural unit (I) in the side chain
3) Comonomer constituent
4) Proportion* (mol%)
5) Type of salt
6) Weight average molecular weight
7) Structural formula
8) Acrylic acid
9) Proportions of monomer containing structural unit (I) in the side chain

① 水溶性重合体番号	② 構造単位（I）を1個以上に含有する水溶性重合体 構造式 ⑦	R¹	R²	③ モノマー成分	④ 比率 * (モル%)	⑤ 塩の種類	⑥ 重量平均分子量
20		-CH₃	-CH₂COONa	⑧ アクリル酸	20	Sodium ナトリウム	33000
21		-CH₃		⑧ アクリル酸	20	Sodium ナトリウム	42000
22		H		⑧ アクリル酸	20	Sodium ナトリウム	87000
23		H		⑧ アクリル酸	20	Sodium ナトリウム	56000
24		-CH₂COONa	-CH₂COONa	—	100	Sodium ナトリウム	570000
25		-CH₂COONa	-CH₂COONa	⑧ アクリル酸	20	Sodium ナトリウム	71000

* 構造単位（I）を1個以上に含有する単量体の比率 ⑨

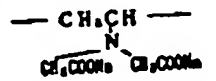
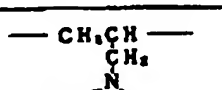
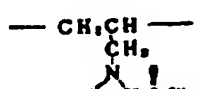
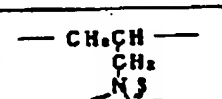
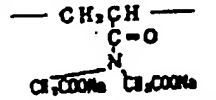
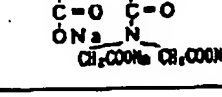
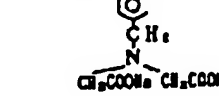
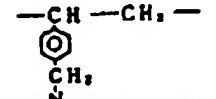
[Table 5]

【0044】

【表5】

Key

1) Water-soluble polymer number
2) Water-soluble polymers containing structural unit (I) in the side chain
3) Comonomer constituent
4) Proportion* (mol%)
5) Type of salt
6) Weight average molecular weight
7) Structural formula
8) Acrylic acid
9) Proportions of monomer containing structural unit (I) in the side chain

① 水溶性重合体番号	② 構造単位（I）を1種類に含有する水溶性重合体 構造式 ⑦	R^1	R^2	③ ﾌﾘｰ成分	④ 比率＊ (mol%)	⑤ 塩の種類	⑥ 重量平均分子量
26		$-CH_2COONa$	$-CH_2COONa$	−	100	Sodium ナトリウム	39000
27		$-CH_2COONa$	CH_2COONa	−	100	Sodium ナトリウム	48000
28		H	$-CH_2P(=O)(ONa)-ONa$	−	100	Sodium ナトリウム	220000
29		H	$-CH_2P(=O)(ONa)-ONa$	−	100	Sodium ナトリウム	100000
30		H	$-C(=S)-NH_2$	−	100	−	74000
31		$-CH_2COONa$	$-CH_2COONa$	−	100	Sodium ナトリウム	88000
32		$-CH_2COONa$	$-CH_2COONa$	−	100	Sodium ナトリウム	2100
33		$-CH_2COONa$	$-CH_2COONa$	−	100	Sodium ナトリウム	3600
34		$-CH_3$	$-CH_2(CHOH)_4CH_2OH$	−	100	−	6900

＊構造単位（I）を1種類に含有する単量体の比率 ⑧

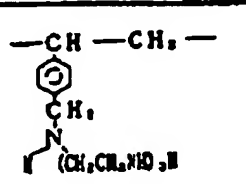
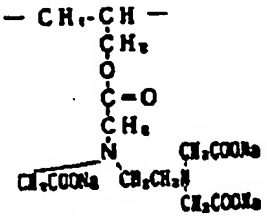
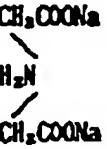
[Table 6]

【0045】

【表6】

Key

1) Water-soluble polymer number
2) Water-soluble polymers containing structural unit (I) in the side chain
3) Comonomer constituent
4) Proportion* (mol%)
5) Type of salt
6) Weight average molecular weight
7) Structural formula
8) Proportions of monomer containing structural unit (I) in the side chain

① 水溶性重合体番号	② 構造単位（I）を側鎖に含有する水溶性重合体			③ コモノマー成分	④ 比率 * (mol%)	⑤ 塩の種類	⑥ 重量平均分子量
	構造式 ⑦	R^1	R^2				
35		H	$-(CH_2CH_2NH)_2H$	-	100	-	11000
36		$-CH_2COONa$		⑧ アクリル酸	20	Sodium ナトリウム	53000

* 構造単位（I）を側鎖に含有する単量体の比率 ⑨

Key
1) Water-soluble polymer number
2) Water-soluble polymers containing structural unit (I) in the side chain
3) Comonomer constituent
4) Proportion* (mol%)
5) Type of salt
6) Weight average molecular weight
7) Structural formula
8) Acrylic acid
9) Proportions of monomer containing structural unit (I) in the side chain

Ⓐ 実験例	Ⓑ 漂白前処理剤	Ⓒ 前処理剤使用量（%対パルプ）	Ⓓ (注1) 過酸化水素消費率(%)	Ⓔ ハンター白色度（%）
1	水溶性重合体1	0.2	71.6	79.8
2	水溶性重合体2	0.2	73.1	78.8
3	水溶性重合体3	0.2	71.9	79.7
4	水溶性重合体4	0.2	73.3	78.9
5	水溶性重合体5	0.2	71.4	79.6
6	水溶性重合体6	0.2	73.3	78.7
7	水溶性重合体7	0.2	71.5	79.8
8	水溶性重合体8	0.2	71.4	79.6
9	水溶性重合体9	0.2	71.2	79.9
10	水溶性重合体10	0.2	71.3	79.6
11	水溶性重合体11	0.2	73.6	78.6
12	水溶性重合体12	0.2	73.5	78.6
13	水溶性重合体13	0.2	73.8	78.9
14	水溶性重合体14	0.2	73.3	78.7
15	水溶性重合体15	0.2	72.2	79.3
16	水溶性重合体16	0.2	72.4	79.3
17	水溶性重合体17	0.2	72.5	79.4
18	水溶性重合体18	0.2	72.5	79.2
19	水溶性重合体19	0.2	72.3	79.3

F

Ⓖ (Note 1)

$$\text{Hydrogen peroxide consumption rate}\ (\%) = \frac{B - C}{B} \times 100$$

B：漂白前の液中の過酸化水素濃度（%）
C：65℃で5時間熱処理漂白後の液中の過酸化水素濃度（%）

[Table 8]

【0054】

40 【表8】

Key

A) Working Example

B) Bleach pretreatment agent

C) Amount of pretreatment agents used (% to pulp)

D) (Note 1) Hydrogen peroxide consumption rate (%)

E) Hunter brightness (%)

F) Water-soluble polymer ...

G) B: Hydrogen peroxide concentration in solution before bleaching (%)
C: Hydrogen peroxide concentration in solution after hot bleach treatment at $65^{\circ}C$ for five hours (%)

A B C D E

実験例	漂白前処理剤	前処理剤使用量(%対パルプ)	(注2)過酸化水素消費率(%)	ハンター白色度(%)
20	水溶性重合体20	0.2	74.3	78.3
21	水溶性重合体21	0.2	74.6	78.3
22	水溶性重合体22	0.2	74.8	78.4
23	水溶性重合体23	0.2	74.3	78.2
24	水溶性重合体24	0.2	71.6	79.8
25	水溶性重合体25	0.2	72.7	79.4
26	水溶性重合体26	0.2	74.4	78.4
27	水溶性重合体27	0.2	74.5	78.3
28	水溶性重合体28	0.2	75.1	77.5
29	水溶性重合体29	0.2	75.0	77.6
30	水溶性重合体30	0.2	75.2	77.7
31	水溶性重合体31	0.2	74.6	78.3
32	水溶性重合体32	0.2	74.1	78.4
33	水溶性重合体33	0.2	74.4	78.2
34	水溶性重合体34	0.2	75.2	77.6
35	水溶性重合体35	0.2	75.3	77.5
36	水溶性重合体36	0.2	74.5	78.5
37	水溶性重合体1	0.05	75.9	77.5
38	水溶性重合体1 水溶性重合体15	0.1 0.1	71.3	79.8

F

G (注2) 過酸化水素消費率：表7 (注1)に同じ

Key

A) Working Example
B) Bleach pretreatment agent
C) Amount of pretreatment agents used (% to pulp)
D) (Note 1) Hydrogen peroxide consumption rate (%)
E) Hunter brightness (%)
F) Water-soluble polymer ...
G) (Note 2) Hydrogen peroxide consumption rate: Identical with that in Table 7 (Note 1)

[0055] [Comparative Examples 1 to 6] The hydrogen peroxide consumption rate and brightness of handsheets were measured just like in Working Example 1 except for the use of the bleach pretreatment agents shown in Table 9. The results are also shown in Table 9.

[0056]

[Table 9]

A B C D E

比較例	漂白前処理剤	前処理剤使用量 (%対パルプ)	(注3) 過酸化水素消費率(%)	ハンター白色度 (%)
1	F ジエチレントリアミン5酢酸ナトリウム (DTPA)	0.2	78.2	74.6
2	G エチレンジアミン4酢酸ナトリウム (EDTA)	0.2	80.0	74.1
3	ジエチレントリアミンペンタメチレンリン酸ナトリウム H (DTPMPA)	0.2	79.1	74.8
4	I トリポリリン酸ナトリウム	0.2	82.2	73.9
5	ポリα-ヒドロキシアクリル酸ナトリウム J (重量平均分子量 125000)	0.2	82.9	74.4
6	ポリアクリル酸ナトリウム K (重量平均分子量 78000)	0.2	77.3	75.9

L (注3) 過酸化水素消費率：表7 (注1)に同じ

Key

A) Comparative Example
B) Bleach pretreatment agent
C) Amount of pretreatment agent used (% to pulp)
D) (Note 3) Hydrogen peroxide consumption rate (%)
E) Hunter brightness (%)
F) Diethylenetriaminepentaacetic acid (DTPA)
G) Ethylenediaminetetraacetate (EDTA)
H) Diethylenetriamine penta(methylenephosphonic acid (DTPMPA)
I) Sodium tripolyphosphoric acid
J) Poly-α-sodium hydroxyacrylate (Weight average molecular weight 125,000)
K) Sodium polyacrylate (Weight average molecular weight 78,000)
L) (Note 3) Hydrogen peroxide consumption rate: Identical with that in Table 7 (Note 1)

[0057]

[Effects of Invention] As mentioned above, wood pulp can be bleached at a high degree in the subsequent bleaching step by the bleach pretreatment method of wood pulp pursuant to the present invention using a comparatively low amount. Furthermore, a high degree of bleach pretreatment of wood pulp can be attained using a pretreatment agent which is inexpensive and which has low toxicity.